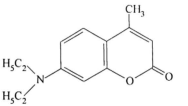
Chapter 2

Experimental

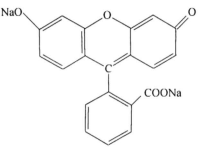
2.1 Preparation of dye-doped PVA films

The laser dyes, Coumarin 460 (C460), Disodium Fluorescein (DF) and Rhodamine 640 perchlorate (R640) (Figure 2.1), were purchased from Exciton Inc., and were used without further purification. The PVA solution was prepared by dissolving poly(vinyl alcohol) (Aldrich, MW = 85,000-146,000) (Table 2.1) in distilled water at 60-80 °C to give a viscous 20 wt% solution. In a typical experiment, 0.0023g of C460 was dissolved in 10 ml of ethanol to give a clear yellow solution of $1x10^{-3}$ M concentration. The ethanol solution was added to the cool colourless PVA solution and the mixture stirred. The volumes range of the dye solution (Table 2.2) was used so that the viscosity of the resulting mixture was not significantly different among the mixtures. When higher concentrations were used, the dyes precipitated from the mixture. A similar procedure was used to prepare the R640/PVA and DF/PVA mixtures. Figure 2.2 shows the PVA solution and the dye doped PVA mixtures.

C460



DF



R640

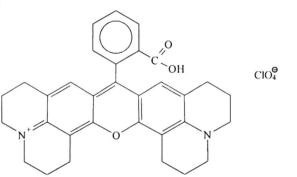


Figure 2.1 Structures of C460, DF and R640.

Molecular Structure	PVA film (15 μm) transmission at 337 nm
$-CH_2\,\underset{\displaystyle OH}{\underset{|}{CH}}\,CH_2-$	99.0%

Table 2.1 Molecular structure and the optical transparency of PVA film.

Dye	Maximum volume percentage of dye solution in PVA (%)	Concentration range in PVA (M)
C460	12.0	5.0×10^{-5} - 3.0×10^{-3}
DF	20.0	2.5×10^{-5} - 5.0×10^{-3}
R640	27.5	8.0×10^{-4} - 2.2×10^{-3}

Table 2.2 Dyes and their doping concentration ranges.

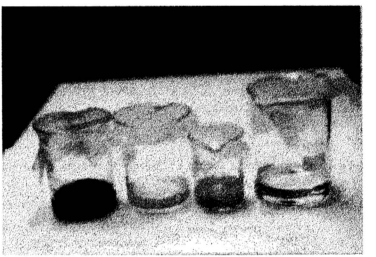


Figure 2.2 Transparent PVA solution and the dye doped PVA mixtures. (From right: PVA, DF/PVA, C460/PVA, R640/PVA)

The dye-doped polymer films were prepared by dipping glass slides into the PVA solution and then allowing the coating to dry. Two types of glass slides, one with a 'frosted' edge (76 x 26 x 1 mm) and the other with an 'as-cut' edge (76 x 26 x 0.95 mm), both of 1.51 refractive index, were used (to be described in section 2.2). After being immersed in the mixture for approximately 1 sec, the slide was taken out and then left to stand horizontally to dry in the air for several hours. The approximate area of the film was ~30 mm x 26 mm (Figure 2.3). The concentration of the dye in the PVA host was estimated to be about 20% higher than that in the original mixture. The thickness of the film, as measured by using a profilometer system was 10-25 μm.

After the laser measurements, the edge of the 'as cut' slide from which the laser beam had exited was polished by using fine sandpaper. For the purpose of discussion, the slides are called 'polished' slides.

The dyes were also doped into PMMA matrices. Commercial-grade high-molecular weight PMMA (MW = 800,000) was dissolved in chloroform to form a moderately viscous mixture, and a chloroform solution of the dye was then added. The slides were dried in a draught-free area; when dried in air, the films were found to be uneven and some were partially opaque. The slow-dried films, of 10-25 μm thickness, flaked after several weeks (Figure 2.4). No flaking was noted with the PVA films even after several months.

A frosted edge slide was coated in separate sections with each of the three dyes. After the first dye had dried to a film, the second was poured onto the slide. The sections were separated from each other by air gaps and there was no overlap (Figure 2.5).

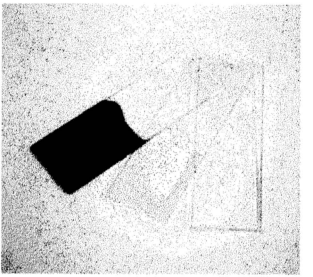


Figure 2.3 Dipped coated dye doped PVA films on glass slides.

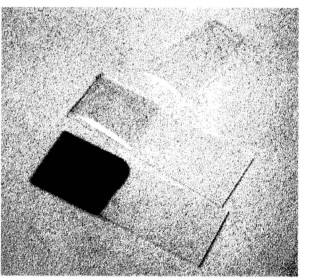


Figure 2.4 Dye doped PMMA films on glass slide and the detached film.

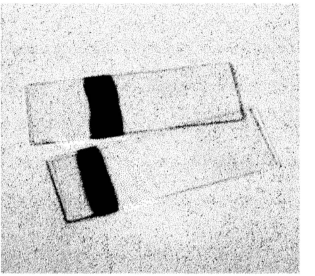


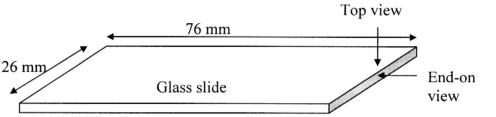
Figure 2.5 Three non-overlapping coatings of C460/PVA, DF/PVA and R640/PVA on a common glass slide.

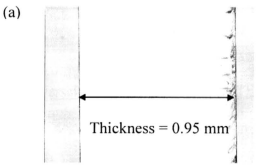
2.2 Description of the edges of the glass slides

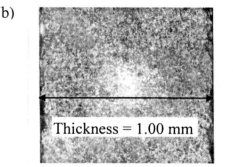
Table 2.3 lists the properties of the two types of support glass slides. The as-cut edge, frosted edge and the polished edge from where the laser emissions exit are shown in Figure 2.6. The images were obtained by using an optical microscope under 50x magnification. The as-cut edge has a smooth surface whereas the frosted edge is rough. The polished edge resembled the sandblasted edge, but it was somewhat less even.

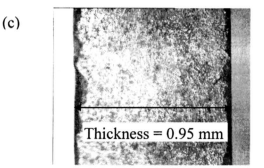
Glass type	Thickness (mm)	Transmittance at 337 nm (%)	Condition of the edge
As-cut edge	0.95	87.0	smooth
Frosted edge	1.00	83.2	rough

Table 2.3 Properties of the glass slides.









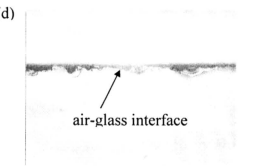


Figure 2.6 End-on view of the glass slide: a transparent as-cut edge (a), a semi-transparent frosted edge (b) and a polished as-cut edge (c). Top view of the polished edge glass slide shows the uneven edge (d).

2.3 Measurements

2.3.1 Excitation apparatus

Two lasers were used as excitation sources for the dye lasers; a Transversely Excited Atmospheric (TEA) nitrogen laser and a Transversely Excitation (TE) nitrogen laser.

Transversely Excited Atmospheric (TEA) nitrogen laser

A smaller pumping laser source, a TEA laser, was constructed based on the two-stage Blumlein circuit (Tou *et al.*, 1996; Tou *et al.*, 1998). The lasing system, whose details are presented in Appendix I (Tou *et al.*, 1999), was examined as a pump source of the dye doped PVA films. The laser was made compact by using a double-fold, two-stage Blumlein circuit, with the dimensions of 25 cm x 17 cm. Aluminium foils and Mylar layers were folded onto the brass electrodes to give the required discharge and dummy capacitance. The laser channel was pre-ionised by aluminium strips protruding above and below the brass electrodes. The operating voltage was set at 4.5-7.5kV to give an output energy of 150-370 μJ. The low energy allow for only part of the full range of the dye to be covered. All measurements were then carried out with the laser system described next. Figure 2.7 shows the photo of the laser system and Figure 2.8 illustrates end-on view of the design.

Figure 2.7 Two-stage Blumlein low voltage TEA nitrogen laser.

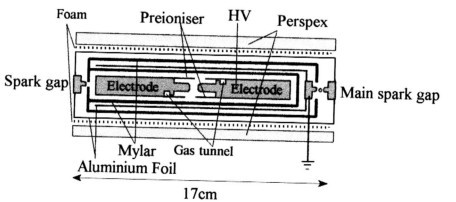


Figure 2.8 End-on view of the TEA laser system.

Transversely Excitation (TE) nitrogen laser

The higher energy laser system was used earlier (Low, *et al.*, 1998). A two-stage Blumlein circuit in the design of the laser ensured an output energy of 450-750 μJ. Three parallel, self-breakdown spark gaps were used for switching the nitrogen laser discharge along with the main triggering spark gap. The capacitor-coupled side pin pre-ionised the three parallel spark gaps which were placed along the trajectory of the laser channel to achieve homogeneous discharge when the spark gaps breakdown simultaneously. At the main laser channel consisting of two brass electrodes, a linear spark array was situated to provide ultra-violet pre-ionisation to enhance the laser output. The maximum output intensity of the laser emission was at ~100 mbar. Figure 2.9 shows the set-up of the laser system and Figure 2.10 shows the cross-sectional view of the structural design.

For the laser measurements, a charging voltage of ~14kV was used to give an output of ~700 μJ at 100 mbar gas pressure. The set-up is shown in Figure 2.11. The laser beam was focused to a line width of 0.03 mm by a cylindrical lens; the length of this line was fixed at 25 mm by two shields. An additional shield was used for the glass slide with separated coatings to define the exposure region. An irradiation power density in excess of $1x10^6$ Watt cm^{-2} was estimated for the 6 ns pumping pulse. The slides were placed on their long edges.

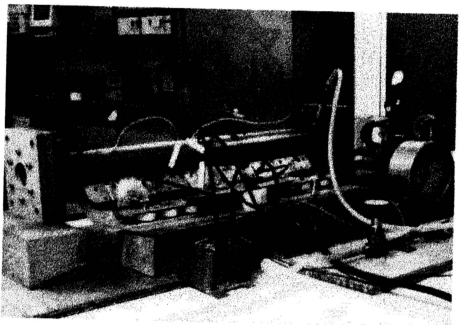


Figure 2.9 The UV pre-ionised two-stage Blumlein TE nitrogen laser employed in the laser measurements.

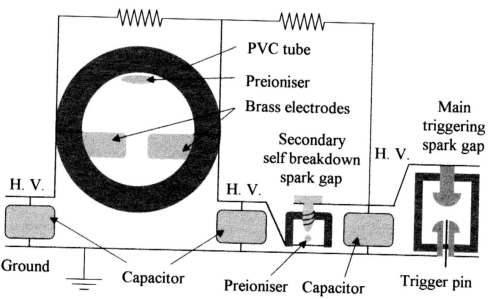


Figure 2.10 Simplified cross-sectional diagram of the UV pre-ionised two-stage Blumlein nitrogen laser.

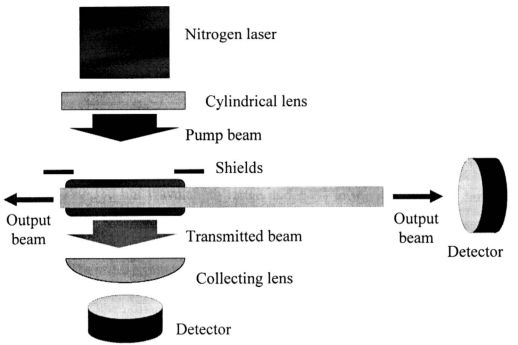


Figure 2.11 Experiment set-up for the excitation and laser emission characterisation.

2.3.2 *Energy measurement*

The input, output and the transmitted energies were measured at two positions (as indicated in Figure 2.11) by using a calibrated joulemeter equipped with a pyroelectric metallic detector head (PE-10, NOVA, Ophir Optronics). The sensitivity, as specified by the manufacturer, was of the order of μJ. The corresponding error was ±8% in the 190-350 nm wavelength range and ±4% in the 400-800 nm range. The wavelengths for red, green and blue energy measurements were set at 460 nm, 550 nm and 640 nm. The measurement of the emission energy was taken at 10 mm from the glass edge as the beam diverged at an angle.

2.3.3 *Spectral analysis*

Laser spectra

The laser spectrum was obtained on a calibrated optical multi-channel analyser (OMA III, EG&G, Princeton Applied Research), which consisted of a diode array detector, a detector interface unit and a host computer. The emission was captured and guided by a UV-VIS optical fibre to the detector unit. Strong and intense emissions required attenuation by a neutral density filter to avoid saturation and also to avoid damage to the photodiode array.

The detector exposure time was set to 1 second for most measurements whereas some weaker emissions required an exposure time of 3 seconds. The detector was configured for a slow mode pixel time scanning (28 μs) for a lower noise level at a default temperature of 5° C; the background attenuation was taken into account by subtracting the background noise.

Absorption spectra

The absorption spectra were recorded using a UV-VIS NIR scanning spectrophotometer of Shimadzu (Model UV-3101 PC). The acquisition mode was pre-set to a fast scanning mode (1600 nm min^{-1}) with a 3 nm slit width, and a sampling interval of 0.5 nm was used for all samples.

Fluorescence spectra

Fluorescence spectra were obtained on a Luminescence spectrometer Perkin-Elmer (LS50B); smoothing by binomial filtering gave good noise reduction with minimum peak distortion. The excitation wavelength was pre-set to 337 nm (which corresponded to the pumping wavelength of nitrogen lasers). The excitation and emission slits were varied between 5-10 nm for analysis of the emission spectra of samples at high signal to noise ratio.

2.3.4 *Beam profile, film and glass slide properties*

The emission beams were captured with a Polaroid camera, and the film quality and the edges of the glass slides were examined by using an optical microscope (Ziess).